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PREVENTING COLOR FORMATION IN GASOLINE

Simon Miron, Texas City, Tex., assignor to The American Oil Company

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This application relates to the use of phenylenediamine-type compounds in hydrocarbons and more particularly in cracked naphthas.

The oxidation stability of oils derived from thermal cracking and catalytic cracking as well as virgin oils containing appreciable amounts of cracked oils is commonly improved by the addition of small amounts of phenylenediamine-type inhibitors or antioxidants. The most widely used of this class of inhibitors is N,N'-di-sec-butyl-p-phenylenediamine. It has been noticed that a color change occurs in cracked oils to which phenylenediamine-type inhibitors have been added, but this color change has normally been too slight to be in any way objectionable.

Recently a new type of sweetening operation has taken hold in the petroleum industry; this so-called inhibitor sweetening process utilizes phenylenediamine-type compounds as catalysts for the oxidation of mercaptans to disulfides. In this process, phenylenediamine compound is added to the sour cracked naphtha and then the diamine-containing naphtha is contacted with aqueous caustic solution and free-oxygen. In this process, much larger amounts of phenylenediamine compound are used than are necessary for the oxidation stabilization of the cracked naphtha. It has been noticed that phenylenediamine inhibitor-sweetened cracked naphtha develops a pinkish color and frequently this color becomes a brownish shade. Under normal circumstances, this color development is not objectionable because the refiner is able to mask the color by adding dyes; most gasolines are dyed to a sufficient degree that modification of the dye formulation permits masking the pinkish or brownish color without a noticeable change in the final color of the dyed gasoline. However, even a slight amount of this pinkish color impairs the saleability of the so-called water-white gasoline. Also, in the case of U. S. Air Force aviation gasoline, the specification color is such a light blue that it is impossible, frequently, to even attempt to mask the pinkish or brownish color present after phenylenediamine sweetening. Thus, even though the phenylenediamine inhibitor sweetening process is very simple and relatively cheap, its use has been limited to the sweetening of cracked naphthas wherein pink or brown color formation can be masked by the use of suitable dyes.

An object of the invention is a process for treating liquid hydrocarbon oils whose oxidation stability has been improved by the addition of phenylenediamine-type inhibitors to prevent the formation of objectionable amounts of color in the product oil. Another object of the invention is a process of phenylenediamine inhibitor sweetening of cracked naphthas under conditions to avoid the formation of color in the sweet oil. Other objects will become apparent in the detailed description of the invention. It has been found that the formation of a pinkish or brownish color in hydrocarbon oils which have been treated with phenylenediamine-type inhibitors can be prevented by adding to the treated oil an aldehyde prior to the formation of objectionable amounts of color

and preferably before the addition of the phenylenediamine inhibitor.

Not all phenylenediamine compounds cause the formation of pinkish or brownish color in the hydrocarbon oil containing them. Nor do all oils discolor even when a phenylenediamine inhibitor, which causes color in another hydrocarbon oil, is dissolved in the particular oil. Furthermore, if free-oxygen is excluded from the hydrocarbon oil, the formation of the color is avoided even though, in the presence of free-oxygen, color would be formed. (It is impractical in any commercial operation to remove dissolved oxygen from hydrocarbon oil and to exclude the presence of free-oxygen in subsequent processing and in storage before final sale to the consumer.)

The phenylenediamine-type compounds which produce the pinkish or brownish color are those in which (*a*) the amino groups are in either the ortho or the para orientation and (*b*) not more than 1 of the amino groups contains an alkyl substituent group. The alkyl group, if present, contains not more than 16 carbon atoms. To illustrate: o-phenylenediamine and p-phenylenediamine (1,2-diaminobenzene and 1,4-diaminobenzene) will produce, under the proper conditions, objectionable amounts of pinkish color in hydrocarbon oil; meta-phenylenediamine (1,3-diaminobenzene) does not produce pinkish color in hydrocarbon oil under the same conditions. The phenylenediamines may contain substituents on the benzene nucleus other than the amino groups.

It is not necessary that the defined objectionable phenylenediamine-type compounds be utilized directly as either oxidation inhibitors or as sweetening catalyst. These compounds may be introduced into the hydrocarbon oil in admixture with other phenylenediamines which are considered as the principal inhibitors or catalysts. For example, commercial grade N,N'-di-sec-butyl-p-phenylenediamine usually contains appreciable amounts of N-sec-butyl-p-phenylenediamine as an impurity. The amount of the mono-substituted amine is sufficient to cause objectionable amounts of pinkish color when the commercial grade inhibitor is utilized in the treatment of cracked naphthas. Examples of the types of phenylenediamines which, under proper conditions, cause the formation of pinkish or brownish color hydrocarbon oil are: o-phenylenediamine, p-phenylenediamine, N-sec-butyl-p-phenylenediamine, N-t-butyl-p-phenylenediamine, N-hexyl-p-phenylenediamine, N-dodecyl-o-phenylenediamine, 1-methyl-3,6-diaminobenzene, and 1,4-dimethyl-3,6-diaminobenzene.

Under the proper conditions, objectionable amounts of color are formed when the phenylenediamine inhibitors are added in very small amounts. For example, in a sour catalytically cracked naphtha, a commercial phenylenediamine, containing on the order of 5 volume percent of objectionable type of phenylenediamine as an impurity, rendered the naphtha unsuitable for use as water-white gasoline or aviation gasoline component when the commercial grade inhibitor was added in an amount of 5 pounds per 1000 barrels of cracked naphtha. In general, the ordinary conventional usages of these phenylenediamine inhibitors is contemplated, for example, from about 0.5 to 10 pounds per 1000 barrels of oil.

The presence of free-oxygen in the oil is necessary to the formation of the color. This color normally is of a pinkish cast, but often turns to a brownish shade. The free-oxygen may be present by solution from the atmosphere, or may be introduced by an air blowing step during inhibitor sweetening of a sour oil.

The oil itself must contain compounds which either

participate in the color imparting product or promote the formation of the color imparting product.

Phenolic compounds are necessary for the formation of color. These phenolic compounds are the phenols and alkylphenols which are normally found in cracked oils or in higher boiling virgin distillates, such as heater oil, from high sulfur crudes. These phenols may be, for example, phenol, cresol, xylenol, ethylphenol, isopropylphenol, octylphenol, nonylphenol, etc. The alkylphenols, wherein the alkyl group is para to the hydroxy group, are the slowest reacting of the phenols. The alkylphenols, where the alkyl is either ortho or meta to the hydroxy, react very rapidly. Only very very slight amounts of phenols need be present in the hydrocarbon oil in order to produce an objectionable color in the phenylenediamine-treated product oil.

Certain classes of hydrocarbons either participate in the reaction or promote the formation of the color bodies when phenols and oxygen are present. The presence of alkylbenzenes and alkylnaphthalenes in a hydrocarbon oil results in the formation of color. Benzene itself is inactive. Toluene and the xylenes give a very slow formation of color. Isopropylbenzene causes a very rapid formation of color.

The alkylcycloparaffins in hydrocarbon oil cause the formation of the pinkish color. The unsubstituted cycloparaffins, such as cyclopentane and cyclohexane are inactive. However, the alkyl substituted cycloparaffins gave a very rapid formation in color. The methylcycloparaffins, such as methylcyclopentane and methylcyclohexane are particularly effective in the formation of color.

As is expected, the olefins, cycloolefins, diolefins, and cyclodiolefins of all types are extremely effective in producing the undesired color when they are present in the hydrocarbon oil.

The temperatures at which the color formation occurs may be described as throughout the atmospheric temperature range. Higher temperatures accelerate the rate at which the color is formed, but if sufficient time is permitted to elapse, the same intensity of color will be formed, regardless of the temperature at which the oil is maintained. In general, color formation will take place at any temperature at which hydrocarbon oils containing phenylenediamine inhibitors are maintained in commercial storage or refining operations.

When the defined phenylenediamine has been added to an oil containing the defined deleterious components, in the presence of free-oxygen, the color formed is pinkish. Normally, over a period of several days, this pinkish color will turn to a brownish shade. It has been found that when alkali metal hydroxide is present, the pinkish color is stabilized, i. e., does not turn brown. The alkali metal hydroxide may be present either as dispersed solid in the oil or may be introduced as an aqueous caustic dispersion during aqueous caustic contacting. Water or aqueous caustic, in the absence of the other necessary conditions, did not form color.

The formation of the objectionable color is avoided by the addition of an aldehyde to the hydrocarbon oil. Addition of the aldehyde to the oil prior to, or substantially simultaneously with the addition of the phenylenediamine prevents the formation of any objectionable color. The color formation is relatively slow even when the conditions appear to be most favorable, for example, sweetening a sour catalytically cracked naphtha; thus the first appreciable amount of color takes from 1 to 2 hours and the total color formation may require as much or more than 24 hours. Some oils may not show appreciable amounts of color until 24 hours have passed. Therefore, it is possible to add the aldehyde to the oil after the phenylenediamine has been introduced. If the aldehyde is added at the time that the first detectable amounts of color are formed, further development of color is prevented.

Apparently, any aldehyde may be used. The alkane aldehydes (alkanal) having not more than about 10 carbon atoms are particularly suitable. For example, formaldehyde, paraformaldehyde, acetaldehyde, and heptaldehyde. The alkene aldehydes (alkenal) having not more than about 10 carbon atoms, are also particularly useful. For example, acrylaldehyde and crotonaldehyde. The cycloalkanals may be used, for example, cyclopentylaldehyde, cyclohexylaldehyde, methylcyclopentylaldehyde, and methylcyclohexylaldehyde. The aldehydes of the benzene series are suitable for the purposes of this invention, for example, benzaldehyde and various alkylbenzaldehydes, such as tolylaldehyde and xylylaldehyde. The mixed aldehydes, wherein the aldehyde appears in the alkyl side chain of a benzene nucleus, for example, phenacetaldehyde. The heterocyclic aldehydes, such as furfural, may be used. However, owing to the polymerizing properties of the furfurals, these are not desirable for other reasons. It is preferred to utilize the alkanals and alkenals having not more than 10 carbon atoms, cycloalkanals, benzaldehyde, and alkylbenzaldehyde, as the aldehydes utilized. Particularly it is preferred to use formaldehyde, paraformaldehyde and benzaldehyde.

The aldehydes are added to the oil in an amount at least sufficient to prevent color formation or further color formation. It appears that about 1 mole of aldehyde is required per mole of the defined color forming phenylenediamine present in the oil. When utilizing the preferred aldehydes for preventing the color formation in cracked oils, in general, the addition of between about 0.01 and 1% by weight of the aldehyde to the inhibited gasoline will be more than sufficient to avoid color formation when using the usual amounts of phenylenediamine inhibitors. However, it is to be understood that a small number of very simple tests will enable those in this art to determine the minimum amounts of aldehyde which must be added to the particular oil containing the particular phenylenediamine in order to prevent the formation of deleterious amounts of color.

Test 1

A sour gasoline range naphtha derived from the catalytic cracking of gas oils using a fluidized silica-alumina catalyst was sweetened by contacting the sour naphtha with aqueous sodium hydroxide solution, separating aqueous phase from the treated naphtha phase, adding 5 pounds of commercial grade N,N'-di-sec-butyl-p-phenylenediamine per 1000 barrels and then blowing compressed air through the inhibited naphtha before passing the inhibited naphtha to storage. In about 24 hours, the naphtha was sweet to the doctor test and had developed a pinkish color which rendered the naphtha completely useless for blending into water-white gasoline.

A sample of the commercial grade N,N'-di-sec-butyl-p-phenylenediamine was carefully fractionated in a laboratory column into a series of fractions, each containing 5 volume percent of the charge. The fractionation was carried out in a micro Podbielniak column at 100 mm. pressure and 10:1 reflux ratio. The distillation curve indicated that the distillation reached a constant boiling point after the first 7 volume percent had been taken overhead.

The first, second, third, fourth overhead fractions, and a sample of the bottoms were utilized in laboratory sweetening of the sour catalytically cracked naphtha. Only the naphtha containing material from the first and second fractions formed the pinkish color.

The first fraction was then analyzed by infrared and also ultimate composition and other physical properties. This analysis indicated that the 7% low boiling portion of the commercial inhibitor was mainly N-sec-butyl-p-phenylenediamine.

Test 2

Since it was most quickly thought that phenols were

the bad actors, cresols derived from catalytic naphtha were dissolved in c. p. benzene and N-sec-butyl-p-phenylenediamine was added to the solution. No color formed in the solution after several days standing. Even the presence of free-oxygen introduced in the solution would not cause color formation.

The addition of 5 volume percent of catalytic naphtha to the benzene solution of phenols and N-sec-butyl-p-phenylenediamine resulted in formation of appreciable amounts of a pinkish color.

Test 3

Under very carefully controlled conditions, it was determined that color would not form in a cresol-containing catalytic naphtha in the presence of N-sec-butyl-p-phenylenediamine when free-oxygen was absent. Permitting the solution to stand exposed to the air resulted in the formation of pinkish color in the oil.

Test 4

As a result of this rather surprising result, a standard test was devised in order to permit a complete investigation of the color-forming phenomenon. For the testing of the various phenylenediamines, catalytic naphtha was used as the hydrocarbon oil. This catalytic naphtha to be tested was first freed of acid oils by two vigorous washings with 10 volume percent of 20% sodium hydroxide solution. This was followed by a wash with distilled water. About 50 ml. of the washed catalytic gasoline was placed in a 100 ml. volumetric flask; 1.0 ml. of the inhibitor stock solution and 1.0 ml. of the phenol or acid oil solution were added. The solution was diluted to 100 ml. with washed catalytic gasoline and was transferred to a clean 4 oz. oil sample bottle. To the bottle was added 1.5 ml. of 2.5% sodium hydroxide solution. The bottle was stoppered, shaken and allowed to stand. A positive test consisted of the development of a distinct pink color within about 24–48 hours.

The acid oil solution was made so that when 1 ml. was diluted to 100 ml. with catalytic naphtha, the resulting solution contained 0.1 weight percent acid oil. The acid oil employed for this solution was derived by acid-springing of a spent caustic solution from the treating plant. The phenylenediamine solution was made up by adding 2.40 gm. to 1000 ml. of benzene; 1 ml. of this solution, when diluted to 100 ml., gave a resulting solution which contained 1 lb. of the phenylenediamine material per 5000 gallons of oil, or 8.40 pounds per 1000 barrels.

Tests with high purity ortho, para and meta-phenylenediamine (diaminobenzene) showed that the meta isomer did not cause color formation whereas the ortho and para isomers did cause color formation. Aniline (aminobenzene) did not cause color formation. Other phenylenediamine compounds were tested. These tests show that the meta oriented diamines did not cause color formation, whereas the ortho and para oriented compounds did cause color formation. (That is, the amino groups in the compounds which did not form color were meta oriented with respect to each other.) However, the tests showed that if both amino groups contained alkyl substituents, no color was formed, regardless of the orientation of the amino groups. Likewise none of the meta oriented phenylenediamines which contained only one alkyl substituent amino group had formed color.

Test 5

In this test, the importance of the presence of a phenolic compound was tested. In this test, various benzene hydrocarbons were added to the dephenolized catalytic naphtha. In these tests, the color forming diaminobenzene was used. Addition of phenol caused color formation. Cresols and xylenols added to the test solution caused color formation. However, those compounds where an alkyl group was para to the hydroxyl group reacted slowly. Very rapid reactions were obtained using ortho-cresol and meta-cresol.

Test 6

In this test, the presence of materials other than phenols phenylenediamine, and free-oxygen was examined. The test solution in these tests was benzene, since no color was formed in a solution in benzene of phenol-free-oxygen and an objectionable phenylenediamine.

Toluene and various xylene isomers, when added to the benzene solution, caused a slow formation of color. Isopropylbenzene added to the solution resulted in a very rapid formation of color.

The addition of various olefins of different types caused, in all cases, a very rapid formation of color.

The addition of unsubstituted cycloparaffins, for example, cyclopentane and cyclohexane, did not produce color in the test solution. However, the addition of substituted cycloparaffins, methylcyclohexane and methylcyclopentane did result in a rapid formation of color.

Test 7

In this test, utilizing the benzene solution, the effect of non-hydrocarbons was examined. Thiophenols and mercaptans, when added to the test solution, did not result in the formation of color. With the exception of diethylether, which gave a very weak indication of color formation, non-hydrocarbon materials did not produce color in the test solution.

Test 8

In this test, the effect of water and caustic was examined. Water added to the test solution did not cause color or have any effect on the color formed when a color forming solution was utilized. However, addition of sodium hydroxide to the system, either as an alcoholic solution or as an aqueous solution, caused the pinkish color to be stable. In the absence of caustic, the pinkish color gradually changes to a brown color. Several days are required for the degeneration of the pinkish color to be complete.

Test 9

In this test, the standard catalytic naphtha solution was utilized. Addition of formaldehyde or paraformaldehyde or benzaldehyde to the test solution prior to the addition of the phenylenediamine completely prevented the formation of the pinkish color. Addition of the aldehydes to the test oil after the phenylenediamine was added also prevented color. Addition of the aldehyde to the solution after the color had reached its maximum did not in any way improve the color of the degraded oil. Addition of the aldehyde to the solution at the time that color first began to show effectively prevented the formation of additional color.

The process of the instant invention is applicable to any hydrocarbon oil system containing the necessary components of phenol and hydrocarbon type, free-oxygen and defined phenylenediamine. However, it is particularly useful in the prevention of color formation during phenylenediamine inhibitor sweetening of cracked naphthas, such as thermally cracked naphtha and catalytically cracked naphtha. In this process, it is preferred to introduce the aldehyde into the hydrocarbon oil immediately before the introduction of the phenylenediamine catalyst. However, equipment limitations on existing units may hinder the addition of the aldehyde prior to the addition of phenylenediamine catalyst. In such case, the aldehyde may be added to the treated oil on the way to storage. It appears that addition of the aldehyde to the treated oil subsequent to one hour after phenylenediamine catalyst addition will usually prevent the formation of any appreciable amount of color in the sweet naphtha.

Thus having described the invention, what is claimed is:

1. In the process of improving the oxidation stability of a hydrocarbon oil containing (1) a phenolic compound, and (2) a member of the class consisting of alkylben-

zenes, alkylcycloparaffins, olefins, cycloolefins, diolefins and cyclodiolefins, which process comprises adding to said oil, in the presence of free-oxygen, a phenylene diamine inhibitor having the amino groups in a non-meta orientation and not more than one amino group having an alkyl substituent group, said alkyl group having not more than 16 carbon atoms, which process is characterized by the formation of a pinkish color in said oil, the improvement which comprises adding an aldehyde to said oil prior to the formation of a significant amount of pinkish color, whereby further formation of pinkish color is prevented.

2. The process of claim 1 wherein said oil is a catalytically cracked naphtha.

3. The process of claim 1 wherein said diamine is N-sec-butyl-p-phenylene diamine.

4. The process of claim 1 wherein said aldehyde is formaldehyde.

5. The process of claim 1 wherein said aldehyde is added in an amount between about 0.01 weight percent and 0.5 weight percent.

6. The process of claim 1 wherein said aldehyde is benzaldehyde.

7. The process of claim 1 wherein said aldehyde is acrylaldehyde.

8. The process of claim 1 wherein said aldehyde is cyclohexylaldehyde.

9. The process of claim 1 wherein said diamine is p-phenylene diamine.

10. The process of claim 1 wherein said diamine is o-phenylene diamine.

11. In the process of phenylenediamine-type inhibitor sweetening of a sour cracked naphtha containing phenols, wherein said naphtha is contacted with aqueous caustic, in the presence of free-oxygen, in the presence of a catalytic amount of a phenylenediamine-type inhibitor containing phenylenediamine component having the amino groups in non-meta orientation and not more than one of said amino groups having an alkyl substituent group, said alkyl group having from 1 to 16 carbon atoms, whereby said naphtha is made sweet to the doctor test and an undesirable color is produced therein, the improvement which comprises adding to the sour naphtha between about 0.01 and 0.5 weight percent of an aldehyde.

12. The process of claim 11 wherein said aldehyde is selected from the class consisting of alkanals and alkenals having not more than 10 carbon atoms, cycloalkanals, benzaldehyde and alkylbenzaldehyde.

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